

## PATENT ABSTRACTS OF JAPAN

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## (54) HEAT-SENSITIVE RECORDING BODY

## (57)Abstract:

PROBLEM TO BE SOLVED: To improve water resistance and sticking resistance by providing a bonding agent composed of a polymer emulsion prepared by emulsion polymerizing a monomer containing at least (meth)acrylonitrile, (meth)acryl ester and ethylene unsaturated carboxylic acid.

SOLUTION: A bonding agent is a polymer emulsion prepared by emulsion polymerizing a monomer containing at least (meth)acrylonitrile, (meth)acryl ester and ethylene unsaturated carboxylic acid. It is essential to use (meth) acrylonitrile as a part of the monomer. At the time of emulsion polymerization, the dissolved oxygen concentration of reactive water phase is kept as the dissolved oxygen concentration in a 0.5% bisulfate soda water solution. The amount of use of a redox polymerization starting agent composed of an oxidizing agent—a reducing agent—an oxidizing agent is used, and the amount of use of the oxidizing agent us 0.001–0.1 pts.wt. to 100 pts.wt. of the total monomer.

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CLAIMS

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[Claim(s)]

[Claim 1] The thermal recording object characterized by being the polymer emulsion obtained on the base material by carrying out the emulsion polymerization of the monomer in which these adhesives contain acrylonitrile, acrylic ester (meta), and ethylene nature unsaturated carboxylic acid at least (meta) in the thermal recording object which prepared the protective layer which contains a leuco color, the heat-sensitive recording layer and pigment containing a coloring agent, and adhesives as a principal component one by one in following condition \*\* and \*\*.

\*\* In case the emulsion polymerization of this monomer is carried out, hold the dissolved oxygen concentration of the system-of-reaction aqueous phase below to the dissolved oxygen concentration in 0.5% sodium bisulfite water solution.

\*\* In case the emulsion polymerization of this monomer is carried out, use the redox polymerization initiator which consists of an oxidizer-reducing-agent-activator, and the amount of this oxidizer used is the 0.001 - 0.1 weight section to this monomer 100 weight section.

[Claim 2] (Meta) The thermal recording object according to claim 1 whose acrylic ester is an ethyl acrylate or butyl acrylate.

[Claim 3] The thermal recording object according to claim 1 or 2 whose ethylene nature unsaturated carboxylic acid is an itaconic acid or a methacrylic acid.

[Claim 4] The thermal recording object according to claim 1 to 3 whose glass transition temperature of the polymerization object of a polymer emulsion is 0-30 degrees C.

[Claim 5] The thermal recording object according to claim 1 to 4 which made water-soluble polyvalent metallic salt contain in a protective layer.

[Claim 6] The thermal recording object according to claim 1 to 5 whose toluene degree of swelling of the toluene insoluble section the toluene fusible part of the desiccation coat of a polymer emulsion is 5% or less, and is 200% or less.

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TECHNICAL FIELD

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[Field of the Invention] This invention relates to the thermal recording object which was especially excellent about the thermal recording object which has a protective layer at a water resisting property and sticking-proof nature (resistance over a thermal recording object sticking to a thermal head at the time of record) on the heat-sensitive recording layer containing a leuco color and a coloring agent.

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PRIOR ART

[Description of the Prior Art] The coloring reaction of the leuco color of colorlessness or light color and an organic or inorganic coloring agent is used, and the thermal recording object which both the coloring matter is contacted with heat and obtained the record image is known well. Comparatively cheaply, since a record device is compactly easy also for the maintenance, this thermal recording object is used in the field broad as facsimile, a record medium of various computers, etc. The thermal recording objects the object for handy terminals, for [ various ] labels, etc. are in the field of the invention. Since the thermal recording object of this application may be used outside of a room in case of rainy weather or may be used under the conditions which contact water also indoors, even if a thermal recording object is excellent in a water resisting property and damp, it does not tear or separate, but the property which was moreover excellent in sticking-proof nature is demanded. The method of the approach of adding a deck-watertight-luminaire-ized agent all over a heat-sensitive recording layer being indicated, and using a hydrophobic giant-molecule emulsion for JP,57-14998,B, JP,57-18520,B, and JP,2-8084,A as adhesives all over a heat-sensitive recording layer is indicated by JP,49-36343,A and JP,54-133352,A in order to improve the water resisting property of a thermal recording object. [0003] It is the purpose which, on the other hand, prevents that a record layer contacts various kinds of solvents, a plasticizer, sebum, and fats and oils, and produce unnecessary coloring or a record image carries out tenebrescence in order to prevent unnecessary coloring by a scratch etc., The technique of preparing the protective layer which used together a water soluble polymer or a water soluble polymer, and deck-watertight-luminaire-ized agents (cross linking agent), such as polyvinyl alcohol, on a heat-sensitive recording layer is proposed variously (for example, JP,59-9909,Y, JP,62-26216,Y, JP,1-17478,B, JP,4-30918,B, JP,4-71716,B, JP,4-77672,B, etc.). Moreover, use of a styrene-acrylonitrile-butyl acrylate copolymer emulsion is proposed by JP,54-128347,A, and use of a polyurethane resin emulsion is proposed by JP,4-22153,B. And since the key objective which prepares this protective layer is grant of the barrier nature to a solvent, a plasticizer, and fats and oils, generally concomitant use with water soluble polymers, such as polyvinyl alcohol and its derivative, or a water soluble polymer, and a deck-watertight-luminaire-ized agent (cross linking agent) is put in practical use. However, with expansion of the field of the invention of a thermal recording object, the class of base material and the configuration of a heat-sensitive recording layer are also diversified, and requests on the thermal recording object with which the both sides of sufficient water resisting property and sticking-proof nature may not be obtained, and a water resisting property and sticking-proof nature have been improved with sufficient balance also by use of the water soluble polymer (concomitant use of a deck-watertight-luminaire-ized agent is included) proposed from the former or a giant-molecule emulsion are mounting.

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TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] The technical problem of this invention is to offer the thermal recording object with which the both sides of a water resisting property and sticking-proof nature have the protective layer improved with sufficient balance.

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## English Translation of JP10-175376A

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MEANS TO SOLVE THE PROBLEM

In thermal recording body provided with protective layer the present invention is based on the thermal recording layer, pigment and adhesive containing leuco dyes and coloring agent on support, and to contain sequentially, thermal recording body including, at a minimum, (meta) the adhesive being acrylonitrile, the polymer emulsion which monomer including acrylate and ethylenic unsaturation carboxylic acid is emulsion polymerized in follows condition ① and ② (meta), and was provided is concerned.

The assumption,

When it makes the ① monomeric substance emulsion polymerize, dissolved oxygen density of system of reaction water phase is held in lower than dissolved oxygen density in 0.5% sodium hydrogensulfite water solution.

When it makes the ② monomeric substance emulsion polymerize, using redox polymerization initiator comprising oxidizer - reducing agent - activator, used amount of the oxidizer is 0.001-0.1 part by weight for 100 monomeric substance part by weight.

Balance was preferable, and both sides of water resistance and スティッキング characteristics resistance found what was improved by using the polymer emulsion which particular monomer was polymerized in particular emulsion polymerization condition in thermal recording body provided with protective layer people of present invention were based on thermal recording layer and pigment and adhesive on support as a result of disputation zealously, and to contain sequentially, and was provided as the adhesive.

[0006]

## MODE FOR CARRYING OUT THE INVENTION

It is acrylonitrile (meta)

In the present invention, it is required to use acrylonitrile as one part of a monomeric substance (meta).

This (meta) acrylonitrile is aimed for a スティッキング resistance-related upgrade, and it is added.

It is acrylate (meta)

Preferred, for example, methyl acrylate, ethyl acrylate, butyl acrylate, acrylic acid -2 - ethylhexyl, methyl methacrylate, ethyl methacrylate, butyl methacrylate, methacrylic acid -2 - ethylhexyl are given 1-12 things carbon number of ester part for acrylate used

in the present invention (meta) , above all, preferably it is ethyl acrylate, butyl acrylate. This (meta) acrylate is aimed for a スティッキング resistance-related upgrade, and it is added.

[0007]

Ethylenic unsaturation carboxylic acid

As for the ethylenic unsaturation carboxylic acid used in the present invention, 3-5 things are preferable carbon number, and, for example, acrylic acid, methacrylic acid, itaconic acid, things such as maleic acid or dicarboxylic acid is given , above all, preferably it is methacrylic acid, itaconic acid.

These ethylenic unsaturation carboxylic acid is added for the purpose of raising mechanical stability of polymer emulsion.

Other monomeric substances

In the present invention, the monomer which is other inter-polymerization possibility can be added in the range that does not lose desired effect.

Butadiene, isoprene, styrene,  $\alpha$  - methylstyrene, methylstyrene, chloroethylene, acrylamide, N- methylolacrylamide are nominated for the example.

Use rate of acrylate and a monomeric substance of ethylenic unsaturation carboxylic acid is not limited the (meta) acrylonitrile to particularly (meta), but, for example, (meta) 50-500 acrylate part by weight, field of 1-50 ethylenic unsaturation carboxylic acid part by weight are desirable for 100 acrylonitrile part by weight (meta).

In use percentage of each monomeric substance such as the above, emulsion polymerization is performed next.

Emulsion polymerization uses each monomeric substance, an emulsifying agent and a redox polymerization initiator, it can be performed in a drainage texture.

[0008]

An emulsifying agent

For an emulsifying agent to apply to the present invention, emulsifying agent of used anionic system and Nonion system can be used conventionally, but when emulsifying agent having radical polymerizing ability is used, it is profitable to スティッキング characteristics of stability and thermal recording body of provided polymer emulsion resistance and prevention of skin fog.

For example of an emulsifying agent having radical polymerizing ability, a thing shown in the following regular expression (1) - (3) is given.

[0009]

[CHEMICAL FORMULA1]

(having 2-20, among equation, R presents an alkyl group of carbon number 5-13, n, value)

[0010]

As for the used amount of an emulsifying agent, 0.5-5.0 % by weight is preferable for all monomeric substances.

It is less than 0.5 % by weight, and mechanical stability of produced polymer emulsion is low, and, even more particularly, polymerization velocity becomes late.

On the contrary, it might fall スティッキング characteristics resistance, water resistance of provided thermal recording body, coloring characteristics when beyond 5.0 % by weight.

[0011]

Redox polymerization initiator

Redox polymerization initiator used with the present invention is redox polymerization initiator comprising oxidizer - reducing agent - activator.

Hydroperoxide and persulfate are used as an oxidizer, for example, as hydroperoxide, as for the cumene hydroperoxide, the tert-butylhydroperoxide, the diisopropyl benzene hydroperoxide, the p-menthane hydroperoxide, 1,1,3,3-tetramethyl butylhydroperoxide, 2,5-2,5-dimethylhexane-dihydroperoxide, potassium persulfate, ammonium persulfate are given as persulfate again.

0.001-0.1 part by weight is preferable as against 100 all monomeric substances part by weight, and used amount of an oxidizer is 0.01-0.1 part by weight.

Chemical resistance of thermal recording body provided with used amount of greater than 0.1 part by weight again, スティッキング characteristics resistance fall, and reaction of extended period is unfavorable to make conclude polymerization with used amount less than 0.001 part by weight without there is not, and reaction concluding only in being necessary.

Glucose, dextrose, ホルムアルデヒドナトリウムスルホキシラート (Rongalite), sodium thiosulfate are used as reducing agent.

Ferrous sulfate, copper sulfate, potassium hexacyanoferrate (III) can be used as activator.

A combination of each initiator system is accepted, and these can determine reducing agent and that used amount of activator appropriately, but preferably preferably 0.001-0.1 part by weight had better usually do 0.001-0.1 part by weight with 0.001-0.01 part by weight for 100 all monomer part by weight in that case of 0.01-0.1 part by weight, activator for 100 all monomer part by weight in that case of reducing agent.

[0012]

Emulsion polymerization

Various monomeric substances, an emulsifying agent and a polymerization initiator are used, and it is emulsion polymerized then subsequently.

This emulsion polymerization makes lower than dissolved oxygen density in 0.5% sodium hydrogensulfite water solution hold dissolved oxygen density of system of reaction water phase, and it is performed.

By means of low dissolved oxygen density, quantity of polymerization initiator can be extremely reduced, besides, the polymer emulsion which is stable can be got in relatively short time.



[0013]

Next,

It is explained in detail about one example in case of emulsion polymerization.

At first,

Deoxygenation deionized water (referred to as which can be left, deoxidation deionized water) and a little emulsifying agent are taught a reaction vessel by deoxidation module.

In addition, in deoxidation deionized water, a monomeric substance and a little emulsifying agent are emulsified particularly, and monomer emulsion is prepared, this is taught drip apparatus.

The reaction vessel and nitrogen gas or bisulfite such as sodium hydrogensulfite or bisulfite potass is added in 2 and did deoxidation of drip device are introduced to the whole fluid, and bubbling is done.

As for the dissolved oxygen density of system of reaction water phase, digestion does electrode by the end of 0.5% sodium hydrogensulfite water solution, till product made in dissolved oxygen densitometer [Eastern Asia electric wave Co., Ltd.] which did calibration is used as 0ppm in the dissolved oxygen density, and 0ppm or thereunder becomes show, the deoxidation continues being operated.

Then subsequently,

Redox polymerization initiator is dissolved in deoxidation deionized water in a reaction vessel.

With the above equipment is finished, for example, less than 50 degrees Celsius are preferable, and, more than decomposition temperature of redox polymerization initiator, it is emulsion polymerized in temperature of less than or equal to 30 degrees Celsius.

This assumption is dissolved oxygen density as it cannot be achieved in the dimension which nitrogen substituted for merely system of reaction like conventional emulsion polymerization method.

This can be achieved or as discussed above, for example, bisulfite is added and because bubbling does a nitrogen gas enough.

It might fall スティッキング characteristics resistance without molecular weight being raised without a lap being worse dissolved oxygen density as for the time of greater than this level, bulking of polymerization initiator and emulsifying agent is needed again.

[0014]

Thus, polyvalent metal salt can be added in polymer emulsion to improve スティッキング characteristics of provided polymer emulsion resistance more.

By this adjunction, metal can build a bridge with the carboxylic acid of polymer, it stops, and スティッキング characteristics resistance are improved.

Polyvalent metal salt to take can be divalence or a metal salt of 3 values, and a thing of water-soluble is preferable.

By way of example only,

Magnesium, zinc, calcium, aluminum, nickel, tin, acetate such as chromium, chloride, sulfate, carbonate are given.

Above all, preferably ammonium carbonate salt of zinc is preferable.

It is desirable for quantity of adjunction of polyvalent metal salt for existing carboxylic acid to use 0.5-1.0 equivalent amount.

In the present invention,

As for the glass transition point of polymer provided by emulsion polymerization, a thing of 0-30 degrees Celsius is preferable.

When glass transition point becomes under 0 degrees Celsius, it is inferior to スティッキング characteristics resistance, it might fall adhesive property when 30 degrees Celsius are exceeded adversely.

Furthermore,

Toluene soluble department of the dry coating is lower than 5%, and it is desirable for polymer emulsion used by the present invention that toluene degree of swelling of insoluble part is lower than 200%.

With more toluene soluble parts of dry coating than 5%, toluene degree of swelling of insoluble part is inferior in スティッキング characteristics of thermal recording body resistance if more than 200%.

[0015]

Leuco dyes

A thing of various public intellect can be used as leuco dyes used with the present invention, but for the operative example, for example, 3,3- bis (p- dimethylaminophenyl) -6 - dimethylamino phthalide, three - dimethylamino -7 - methoxy full Oran, three - diethylamino -6 - methoxy full Oran, three - diethylamino -6 - carbonyl -7 - chlorofull Oran, three 6,7- diethylamino - dimethyl full Oran, three - (N- ethyl -p- toluidino) -7 - carbonyl full Oran, three - diethylamino -7-N- acetyl -N- methylamino full Oran, three - diethylamino -7-N- methylamino full Oran, three - diethylamino -7-N- diethylamino full Oran, three - (N- ethyl -p- toluidino) -6 - carbonyl -7 - anilino full Oran, three - (N- ethyl -p- toluidino) -6 - carbonyl -7 - (p- toluidino) full Oran, three - diethylamino -6 - carbonyl -7 - anilino full Oran, three - di(n- butyl) amino -6 - carbonyl -7 - anilino full Oran, three - (N- ethyl -N- isoamyl amino) -6 - carbonyl -7 - anilino full Oran, three - (N- cyclohexyl -N- methylamino) -6 - carbonyl -7 - anilino full Oran, Three - dimethylamino -6 - carbonyl -7 - キシリジノフルオラン, three - diethylamino -7 - (o- chloroanilino) full Oran, three - di(n- butyl) amino -7 - (o- chloroanilino) full Oran, three - pyrrolidino -6 - carbonyl -7-p- butyl anilino full Oran are given.

In addition,

These leuco dyes can use more than two kinds together if necessary.

[0016]

Coloring agent

It is responded with leuco dyes, and, for color development coloring agent to be able to place, a thing of various public intellect is available, for example, 4,4'-sec-re-den diphenol, four-phenylphenol, 4,4'-dihydroxy-diphenyl-methane, 4,4'-isopropylidene diphenol, 4,4'-cyclohexylidene bisphenol, 4,4 1,3-'-[phenylenebis (sulfonylurea derivatives such as one-methylethylidene)] bisphenol, 4,4 1,3-'-(dimethyl re-den) bisphenol, 4,4'-dihydroxy diphenylsulphon, 2,4'-dihydroxy diphenylsulphon, four-hydroxy-4'-methoxy diphenylsulphon, four-hydroxy-4'-isopropoxy diphenylsulphon, four-hydroxy-3', four'-trimethylene diphenylsulphon, four-hydroxy-3', four'-tetramethylene diphenylsulphon, 3,4-dihydroxy-4'-carbonyl diphenylsulphon, three bis(-allyl-4-hydroxyphenyl) sulfone, four-hydroxybenzoic acid-p-methoxybenzyl, Novolak pattern phenol resin, phenolic chemical agent such as phenol polymer, 4,4'-bis(p-toluenesulfonyl aminocarbonyl amine) diphenyl-methane)

Zinc salt such as aromatic carboxylic acid such as 3,5-dimethyl-4-hydroxybenzoic acid, three-isopropyl salicylic acid, 3,5-di-tert-butyl salicylic acid, three-benzil salicylic acid, three-( $\alpha$ -methylbenzyl) salicylic acid, three-chloro-5-( $\alpha$ -methylbenzyl) salicylic acid, three-phenyl-5-( $\alpha$ ,  $\alpha$ -dimethylbenzyl) salicylic acid, 3,5-di- $\alpha$ -methylbenzyl salicylic acid, four-(2-p-methoxyphenoxy ethoxy) salicylic acid, four-(3-p-tolylsulfonyl propyl Oki ti) salicylic acid is given.

It is superior, and, in these, 4,4'-screw (p-toluenesulfonyl aminocarbonyl amine) diphenyl-methane is desirable for keeping quality of record image.

In addition,

Of course these coloring agent can use more than two kinds together if necessary, too.  
[0017]

Use percentage

With the thing which the leuco dyes and use percentage of coloring agent accept leuco dyes and kind of coloring agent to use, and should be selected appropriately, it is not limited to particularly, but preferably coloring agent of 2-6 part by weight dimension is used 1-10 part by weight dimension for one leuco dyes part by weight.

In addition,

According to the present invention, sensitizing agent can be used together depending on purpose.

For example, stearic acid amide, stearic acid methylenebis amide, oleic amide, palmitin acid amide, fatty amide, 2,2'-methylenebis (four-carbonyl-6-tert-butylphenol) such as Lasi fatty amide, 1,2-di(three-methylphenoxy) ethane, 1,2-diphenoxy ethane, one-phenoxy-2-(four-methylphenoxy) ethane, paraben Jill biphenyl, naphthyl benzyl ether, benzil-4-methylthio phenyl ether, one-hydroxy-2-naphthoic acid phenyl ester, oxalic acid dibenzyl ester, oxalic acid-di-p-carbonyl benzyl ester, oxalic acid-di-p-chloro benzyl ester, terephthalic acid dimethylester, terephthalic acid dibutyl esters are embarrassed, and, for an operative example of sensitizing agent, di phtalate benzyl ester,

isophthalic acid dibutyl esters, one - hydroxynaphthoic acid phenyl ester and heat fusibility substance of various dye intellect are given.

Above all, 1,2- di (three - methylphenoxy) ethane, 1,2- diphenoxy ethane are particularly preferable.

Used amount of sensitizing agent is not limited in particular, but, in general terms, what is regulated in the range of less than 400 part by weight dimension as against 100 coloring agent part by weight is desirable.

[0018]

It does not interfere to add a keeping quality conditioner to improve keeping quality of the thermal recording layer more at all.

For such a keeping quality conditioner, for example, 4,4'-butylidene bis (6-tert-butyl-3-methylphenol), 2,2'-methylenebis (four-ethyl-6-tert-butylphenol), 2,4-di-tert-butyl-3-methylphenol, 1,1,3-tris (two-carbinyl-4-hydroxy-5-tert-butylphenyl) butane, 1,1,3-tris (five-cyclohexyl-4-hydroxy-2-methylphenyl) butane, hindered phenols such as 1,3,5-tris (2,6-4-tert-butyl-3-hydroxy-dimethylbenzyl) isocyanuric acid, four- (two 1,2-carbinyl-epoxyethyl) diphenyl sulfone, four- (two 1,2-ethyl-epoxyethyl) diphenyl sulfone, four- (two 3,4-carbinyl-epoxy butyl) diphenyl sulfone, four- (two 2,3-carbinyl-epoxy butyl) diphenyl sulfone, four- (two 1,2-carbinyl-epoxyethyl Oki ti) diphenyl sulfone, four- (two 2,3-carbinyl-epoxy butyl Oki ti) diphenyl sulfone, four- (two 1,2-carbinyl-glycidyl Oki ti) diphenyl sulfone,

Diphenyl sulfone derivatives such as four- (two-carbinyl-glycidyl Oki ti) -2', four'-dimethyl diphenyl sulfone, four- (two-carbinyl-glycidyl Oki ti) -2', four'-dichloro diphenyl sulfone, four- (two-carbinyl-glycidyl Oki ti methoxy) diphenyl sulfone, four- (two-carbinyl-glycidyl Oki ti) -4'- (p-methoxy benzyloxy) diphenyl sulfone are given.

Of course,

Is not limited by these, in addition, compounds as necessary more than two kinds can be used together.

[0019]

These leuco dyes, coloring agent, sensitizing agent, a keeping quality conditioner use water as dispersive medium with in respectiveness or leuco dyes respectively, by various wet grinding mill such as length pattern or broadside sand mill, an atto cigarette lighter, ball mill, common business oriented language mil, it is scattered with surface active agent other than the water-soluble polymer chemical agent which seems to be polyacrylamide, polyvinylpyrrolidone, polyvinyl alcohol, carboxymethyl-cellulose, styrene - maleic anhydride copolymer salt and those derivative, after having done with fluid dispersion, is used as preparation of thermal recording layer business coating.

In the present invention

Bonding adhesive, naught airplane or organic pigment, waxes, metallic soap can give UV absorber, a keeping quality conditioner, fluorescent dye, colorant for materials comprising

the thermal recording layer else as more necessary.

[0020]

For example, polyvinyl alcohol, carboxyl group degeneration polyvinyl alcohol, butyral can use water-dispersibility resin such as polyvinyl alcohol, acetoacetyl radical degeneration polyvinyl alcohol, cation degeneration polyvinyl alcohol, sulfone radical degeneration polyvinyl alcohol, silicon degeneration polyvinyl alcohol, amyllum and the derivative, casein, methyl cellulose, hydroxyethyl cellulose, hydroxy methyl cellulose, polyvinylpyrrolidone, polyacrylate, poly acryl flax id, salt of styrene - maleic anhydride copolymer, salt of methyl vinyl ether - maleic anhydride copolymer, aquaresin such as salt of iso propylene - maleic anhydride copolymer, styrene - butadiene latex, vinyl acetate - acrylate copolymerization emulsion, polyurethane emulsion, polyvinylchloride emulsion, polyvinylidene chloride emulsion, methacrylate copolymerization emulsion, acrylate copolymer emulsion as an operative example of bonding adhesive not to mention the above-mentioned polymer emulsion.

[0021]

For example, for pigment, clay, calcined clay, porcelain clay, calcium carbonate, magnesium carbonate, purified talc, silica, diatomaceous earth, a synthetic aluminum silicate, zinc oxide, titania, aluminium hydroxide, barium sulfate, surface finishing can give organic system resin impalpable powder such as inorganic system impalpable powder such as done calcium carbonate or silica and urea - formalin resin, styrene - methacrylic acid copolymer, polystyrene resin.

For wax, stearic acid amide, higher fatty acid amide such as ethylenebis stearic acid amide and higher fatty acid ester are given other than paraffin wax, カルナバロウワックス, microcrystallin wax, polyethylene wax.

In the present invention,

The particular bonding adhesive is applied to protective layer, but, in the limit that does not lose desired effect of the present invention, adhesive of various duke intellect can be used together, for example, amyllum, hydroxyethyl cellulose, methyl cellulose, carboxymethyl-cellulose, gelatine, casein, gum arabic, polyvinyl alcohol, diisobutylene - maleic anhydride copolymer salt, styrene - maleic anhydride copolymer salt, ethylene - acrylic acid copolymer salt, styrene - acrylic acid copolymer salt, styrene - butadiene copolymer emulsion can be used.

[0022]

Water resistant additive such as glyoxal, methylol melamine, ammonium persulfate, persulfuric acid soda, ferric chloride, magnesium chloride, boric acid, ammonium chloride, zirconium carbonate ammonium may be added by the end of coating fluid for protective layer if necessary.

In addition,

Various auxiliary such as water-solubility polyvalence metal salt such as zinc stearate,

calcium stearate, polyethylene wax, カルナバロウ, paraffin wax, slip additive such as ester wax, surface-tension modifier such as ジオクチルスルフォコハク acid sodium, antifoamer, potassium alum or aluminium acetate, benzophenone system, UV absorber such as triazole series, fluorescent dye, coloration color can be added appropriately.

In addition,

Usable support is not confined to the present invention in particular, can be generally used as support of thermal recording body conventionally.

By way of example only,

Besides, paper such as pigment coated paper, transparence or the synthetic resin film that is semitransparent, synthetic paper are given acidic paper or neutral paper.

[0023]

Is not limited to about the thermal recording layer and formation manner of protective layer particularly, therefore, it can be formed in technology of the common knowledge usage conventionally, for example, preferably it is desirable in dry weight with protective layer business coating fluid 3-12g/m<sup>2</sup> 2-15g/m<sup>2</sup> in dry weight with thermal recording layer business coating fluid by suitable application methods such as an air-knife coating, fin bar bulldozing blade coating, pure bulldozing blade coating, rod bulldozing blade coating, short circuit dwell coating, curtain coating, die coating, a micro gravure coating again 0.5-7.0g/m<sup>2</sup>, that swabbing dries for the purpose of preferably it being in field of 1.0-4.0g/m<sup>2</sup>.

The thermal recording layer and opposite side are provided with a backing layer in thermal recording body of the present invention if necessary, correction of Karl can be planned.

Coating compositions of a backing layer (the back coat layer) and a coating formula may utilize a thing same as protective layer, and coating quantity, resin / pigment ratio are changed as necessary, and it does not interfere.

Furthermore,

It does not interfere to do a variety of transformation provided with the undercoat layer with the thermal recording layer if necessary at all.

After having provided with each sheaf, super calender disposal is given, picture quality, image density can be improved.

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3. In the drawings, any words are not translated.

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EXAMPLE

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[Example] Although an example explains this invention further below, this invention is not limited to these examples. In addition, the "section" in an example, and "%", unless it mentions specially, the "weight section" and "% of the weight" are shown, respectively.

They are meta-chestnut ROKISHI polyethylene-glycol-2-ethylhexyl sulfo succinic-acid soda (polymerization degree of polyethylene glycol = 15) 1.5g, and a ferrous sulfate as an emulsifier to the 1l. flask equipped with the manufacture stirring equipment of an example 1 \*\* polymer emulsion, a thermometer, the capacitor, the dropping funnel, the nitrogen gas vent pipe, and an oxygen analyzer's electrode. 0.002g and water 200g was taught. The dissolved oxygen concentration at this time was 5-7 ppm. It is butyl acrylate to a 1l. beaker independently. 150g, 200g of ethyl acrylates, acrylonitrile 150g, methacrylic acid 10g, meta-chestnut ROKISHI polyethylene-glycol-2-ethylhexyl sulfo succinic-acid soda (polymerization degree of polyethylene glycol = 15) 1.5g, and water 228g was taught and it emulsified by the homomixer. The oxygen density at this time was 8-9 ppm. When the deoxidized nitrogen gas was blown into the beaker and flask containing a monomer emulsification object at 50-100ml a rate for /for 2 hours, the dissolved oxygen concentration meter which proofread to zero in the sodium bisulfite water solution 0.5% showed 0 ppm to them. A monomer emulsification object, 0.3% water solution of a tert-butyl hydroperoxide after the dissolved oxygen concentration of a both system is set to 0 ppm or less 20g and 0.5% water solution of sodium formaldehyde sulfoxylate 20g was dropped in the flask over 3 hours. In the meantime, the temperature of a system was kept at 30-34 degrees C. After dropping termination, it held to this temperature for 1 hour, and riped. 10% caustic alkali of sodium Water was added and the polymer emulsion was obtained so that 5g might be added and solid concentration might become 45% after neutralizing a system.

[0025] \*\* A liquid preparation 3-JI (n-butyl) amino-6-methyl-7-anilino fluoran The 15 sections, 1, 2-JI (3-methylphenoxy) ethane The 20 sections, 5% water solution of methyl cellulose The five sections and water The constituent which consists of the 60 sections was ground until mean particle diameter was set to 1.0 micrometers by the sand mill, and A liquid was obtained.

\*\* B liquid preparation 4, 4'-isopropylidene diphenol The 35 sections, 5% water solution of methyl cellulose The five sections and water The constituent which consists of the 60 sections was ground until mean particle diameter was set to 1.0 micrometers by the sand mill, and B liquid was obtained.

\*\* Preparation A liquid of the coating liquid for heat-sensitive recording layers The 100 sections, B liquid The 100 sections, 10% water solution of polyvinyl alcohol (trade name-VA110, Kuraray Co., Ltd. make) The 100 sections, precipitated calcium carbonate The ten sections and water The constituent which consists of the 50 sections was mixed and stirred, and the coating liquid for heat-sensitive recording layers was obtained.

\*\* The preparation kaolin (trade name: HG clay, made in Huber) 60 section of the coating liquid for protective layers, the polymer emulsion (45% of solid concentration) 70 section obtained by the above-mentioned \*\*, 30% dispersion liquid of zinc stearate The 25 sections, 5% water solution of sodium dioctyl sulfosuccinate The five sections and water The constituent which consists of the 300 sections was mixed and stirred, and the coating liquid for protective layers was obtained.

\*\* After having carried out sequential spreading desiccation so that the coverage after drying the coating liquid for heat-sensitive recording layers and the coating liquid for protective layers might serve as 5 g/m<sup>2</sup> and 3 g/m<sup>2</sup>, and preparing a heat-sensitive recording layer and a protective layer in one side of the paper of fine quality of production basis-weight 65 g/m<sup>2</sup> of a thermal recording object, super calender processing was carried out and the thermal recording object was acquired.

[0026] Meta-chestnut ROKISHI polyethylene-glycol-2-ethylhexyl sulfo succinic-acid soda taught to the flask and the beaker as an emulsifier in manufacture of \*\* polymer emulsion of example 2 example 1 Instead of 1.5g, it is sodium dodecylbenzenesulfonate as an emulsifier to a flask. The thermal recording object was acquired like the example 1 except having used 1.5g [ of sodium dodecylbenzenesulfonate ], and polyoxyethylene lauryl ether (polymerization degree of ethylene oxide = 50) 15g for 1.5g and a beaker as an emulsifier.

[0027] It sets to manufacture of \*\* polymer emulsion of example 3 example 1, and is 0.3% water solution of a tert-butyl hydroperoxide. Instead of 20g, it is 0.15% water solution of cumene hydroperoxide. 10g and 0.1% water solution of ammonium persulfate The thermal recording object was acquired like the example 1 except having used 10g.

[0028] In manufacture of \*\* polymer emulsion of example 4 example 1, the thermal recording object was acquired like the example 1 in the obtained polymer emulsion except having added 5g of 10% water solutions of calcium acetate further.

[0029] It sets to manufacture of \*\* polymer emulsion of example 5 example 1, and is a methacrylic acid. It is an itaconic acid instead of 10g. The thermal recording object was acquired like the example 1 except having used 10g.

[0030] In \*\*B liquid preparation of example 6 example 1, the thermal recording object was acquired like the example 1 except having used 4-hydroxy-4'-isopropoxy diphenylsulfone instead of 4 and 4'-isopropylidene diphenol.

[0031] In \*\*B liquid preparation of example 7 example 1, the thermal recording object was acquired like the example 1 except having used 4 and 4'-screw (p-toluenesulfonyl amino carbonyl amine) diphenylmethane instead of 4 and 4'-isopropylidene diphenol.

[0032] In production of \*\* thermal recording object of example 8 example 1, the thermal recording object was acquired like the example 1 except having used the synthetic paper (trade name: YUPO FPH-80, Oji-Yuka Synthetic Paper make) instead of paper of fine quality as a base material.

[0033] In production of \*\* thermal recording object of example 9 example 1, the thermal recording object was acquired like the example 1 except having used the 75-micrometer PET film (Teijin make) instead of paper of fine quality as a base material.

[0034] It sets to manufacture of \*\* polymer emulsion of example of comparison 1 example 1, and is acrylonitrile. It is butyl acrylate instead of 150g. The thermal recording object was acquired like the example 1 except having used 150g.

[0035] It sets to manufacture of \*\* polymer emulsion of example of comparison 2 example 1, and is butyl acrylate. 150g and ethyl acrylate It is styrene instead of 200g. The thermal recording object was acquired like the example 1 except having used 150g and butadiene 200g.

[0036] It sets to manufacture of \*\* polymer emulsion of example of comparison 3 example 1, and is 0.3% water solution of a tert-butyl hydroperoxide. 20g and 0.5% water solution of sodium formaldehyde sulfoxylate Instead of 20g, it is 5% water solution of a tert-butyl hydroperoxide. 20g and 5% water solution of sodium formaldehyde sulfoxylate The thermal recording object was acquired like the example 1 except having used 20g.

[0037] In manufacture of \*\* polymer emulsion of example of comparison 4 example 1, the thermal recording object was acquired like the example 1 except having manufactured the polymer emulsion, without blowing nitrogen gas into the beaker and flask containing a monomer emulsification object.

[0038] It sets to preparation of the coating liquid for \*\* protective layers of example of comparison 5 example 1, and is a polymer emulsion. It is 10% water solution of polyvinyl alcohol (trade name-VA117, Kuraray Co., Ltd. make) instead of the 70 sections. The thermal recording object was acquired like the example 1 using the 300 sections except having made water into the



70 sections from the 300 sections.

[0039] Set to preparation of the coating liquid for \*\* protective layers of example of comparison 6 example 1. Polymer emulsion It is 10% water solution of polyvinyl alcohol (trade name-VA117, Kuraray Co., Ltd. make) instead of the 70 sections. Using the 300 sections, the addition of water was subtracted from the 300 sections in the 70 sections, and the thermal recording object was further acquired like the example 1 in production of \*\* thermal recording object except having used the 75-micrometer PET film (Teijin make) instead of paper of fine quality as a base material. The following evaluations were performed about the polymer emulsion and thermal recording object which were acquired in this way, and the obtained result was shown in Table 1 and 2, respectively.

[0040] 45% of evaluation [viscosity of polymer emulsion] solid concentration of a polymer emulsion and the viscosity of the polymer emulsion in 30 degrees C were measured in the Brookfield viscometer.

[pH of a polymer emulsion] pH of 45% of solid concentration and the polymer emulsion in 25 degrees C was measured with the pH meter (Horiba, Ltd. make).

[Glass transition point] The glass transition point of the polymer film obtained by applying a polymer emulsion on aluminum foil and drying (60 degrees C, 5-hour desiccation) was measured with the differential thermal analyzer (the SEIKO electronic industry company make) so that the thickness after desiccation might be set to about 50 micrometers.

[Toluene-proof nature] While dipping the 3cmx3cm polymer film (W) used on the occasion of measurement of the above-mentioned glass transition point in toluene (10ml and 25 degrees C) for 24 hours, measuring the amount of polymer films (A) by which elution was carried out to toluene and calculating A/W, the amount of polymer films (B) swollen in toluene was measured, and B/W was calculated.

[0041] In order to evaluate extent of evaluation [whiteness degree] natural complexion fogging of a thermal recording object, the whiteness degree of a thermal recording object was measured with hunter white chromoscope.

[Coloring concentration] A sensible-heat simulator (the Okura electrical machinery company make, TH-PMD) is used, and it is impression energy. It recorded on the thermal recording object by 0.4 mj/dot, and the coloring concentration of the obtained record image was measured with the Macbeth densimeter (made in Macbeth, RD-100 R form).

[Head \*\*] A sensible-heat simulator (the Okura electrical machinery company make, TH-PMD) is used, and it is impression energy. After carrying out continuation record to a thermal recording object with a die length of about 10m on condition that 0.4 mj/dot, \*\* which adhered on the head was observed.

O : there is no \*\*\*\*\*.

O : although \*\* has adhered slightly, it is completely convenient to printing.

\*\* : There is a little much \*\*\*\*\* and it poses a problem depending on demand quality.

x : There is much \*\*\*\*\* , and it cannot produce and put trouble in practical use in printing, either.

[Water resisting property] It takes out, after making a thermal recording object underwater immersed for 1 minute, and protection stratification planes are removed after superposition and desiccation.

O : a protection stratification plane separates convenient.

x : When removing, somewhere in protective layers, record layers, and base materials are destroyed, or exfoliate.

[Sticking-proof nature] A sensible-heat simulator (the Okura electrical machinery company make, TH-PMD) is used, and it is impression energy. After recording on a thermal recording object by 0.4 mj/dot, the degree of sticking generated in the protective layer was judged visually.

O : there is almost no sticking.

O : although sticking is accepted for a while, it is satisfactory practically.

x : Sticking cannot put in practical use by having generated mostly.

[0042]

[Table 1]

重合体エマ ルジョン	固形濃度 (%)	粘度 (cps)	pH	ガラス 転移点	耐トルエン性	
					溶出(%)	膨潤(%)
実施例1	45	80	7.8	11℃	1.0	150
実施例2	45	210	8.0	10℃	3.1	180
実施例3	45	50	7.9	9℃	1.0	110
実施例4	45	50	8.0	10℃	0.5	90
実施例5	45	40	7.1	8℃	0.6	120
比較例1	45	50	8.5	-15℃	15	600
比較例2	45	70	7.9	0℃	10	500
比較例3	45	130	8.8	10℃	7.5	510
比較例4	重合体エマルジョン得られず					

[0043]

[Table 2]

	白色度 (%)	発色濃度	ヘッド粕	耐水性	耐スティッ キング性
実施例1	82.1	1.20	◎	○	◎
実施例2	81.8	1.22	○	○	○
実施例3	82.3	1.21	◎	○	◎
実施例4	83.1	1.18	◎	○	◎
実施例5	82.5	1.19	◎	○	◎
実施例6	83.5	1.25	◎	○	◎
実施例7	80.8	1.19	◎	○	◎
実施例8	83.7	1.28	◎	○	◎
実施例9	80.5	1.13	○	○	○
比較例1	80.2	1.23	×	○	×
比較例2	79.8	1.26	×	○	×
比較例3	80.5	1.22	×	○	×
比較例4	79.3	1.21	×	○	×
比較例5	79.0	1.08	○	×	○
比較例6	80.4	1.12	△	×	×

[Translation done.]

\* NOTICES \*

JPO and NCIP are not responsible for any damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.\*\*\*\* shows the word which can not be translated.

3.In the drawings, any words are not translated.

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EFFECT OF THE INVENTION

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[Effect of the Invention] According to this invention, the thermal recording object excellent in the both sides of a water resisting property and sticking-proof nature is offered.

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[Translation done.]